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AN APPARENT HIGH PRESSURE DUE TO ADSORPTION, THE HEAT OF ADSORPTION, AND THE DENSITY OF GAS-MASK CHARCOALS

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A knowledge of the volume of the pores, and of the density of the active carbon in gas-mask charcoal, is of importance in connection with the working out of a theory in regard to the efficiency of charcoal as an adsorbent of gases, so the problem of the determination of the pore volume was given to us by the National Research Council in connection with the work of problem 108. We have discovered that factors which have hitherto been unsuspected complicate such a determination, the interesting new phenomenon being that the volume of the liquid absorbed depends upon the physical properties of the liquid. Thus it has been found that the volume of water or of an organic liquid taken up by a definite weight of any charcoal which is very efficient as an adsorber of gases, increases as the compressibility of the liquid increases, or as either the viscosity or the surface tension decreases. This effect decreases as the adsorptive capacity decreases, and entirely disappears when the charcoal becomes valueless as a gas adsorbent.

While effects of the same general order were found whether the charcoal was put in the liquid directly from the canisters or from the bottles in which it was stored, or only after an extensive "outgassing" or heating and pumping out of the gases contained in it, concordant results were obtained only by the latter procedure. This is a well-known method for cleaning the surface of the charcoal, and the only new features introduced were those which concerned the completeness of the outgassing. The tube containing the charcoal was first exhausted by a rapid mercury condensation pump, and then heated up very slowly in vacuo until the temperature finally reached 600° C., keeping the pump running. The heating and evacuating usually continued for two days, though this time varied greatly with the nature of the charcoal, and was only ended when the pressure in the system fell to one ten-thousandth of a millimeter at this high temperature,

and remained of that order for about six hours. The tube was sealed off while still at 600°, and was then opened under the hot liquid which had just been boiled to drive off dissolved gases. In some cases the charcoal was treated with the vapor of the liquid while it was still in the vacuum apparatus, and was then subjected to a second outgassing. It was found that it was not sufficient to reduce the pressure to 0.0001 mm. but that this low pressure had to be maintained for hours, if concordant results were to be obtained. Those who are familiar with vacuum work will realize that when a bulb almost completely filled with active charcoal is kept at 0.0001 mm. for hours at 600° C., a very low pressure when the temperature is considered, and is sealed off at this temperature and pressure, the pressure on cooling will fall to an exceedingly low value. It is probable that this pressure is much lower than can be obtained with the extremely efficient condensation pumps, that is, the pressure is probably lower than has ever been measured.

A few of the results obtained by us for a high-grade, steam-activated charcoal (E 602), a 47.2 minute charcoal as determined by the accelerated chlorpicrin test, or about 700 minutes by the ordinary test, are given in table 1. The densities given here are those which the carbon would have if it filled all the space not occupied by the liquid, and if the liquids were incompressible. The densities given are the averages of very closely agreeing values.

TABLE 1

DENSITY AND PORE-VOLUME DETERMINATIONS FOR A STEAM-ACTIVATED COCOANUT SHELL GAS-MASK CHARCOAL (DATA AT 20° C.)

1 LIQUID	2 DENSITY	3 PORE VOLUME IN 1 CU. CM.	4 PER CENT COMPRESSED 12000 ATMOSPHERES[1]	5 SURFACE TENSION DYNES PER CM.	6 VISCOSITY IN ABSOLUTE UNITS
Mercury	0.865			57.0	
Water	1.843	0.534	20.51	72.8	0.0101
Propyl alcohol	1.960	0.559	22.93	23.7	0.0223
Chloroform	1.992	0.566		27.13	0.0057
Benzene	2.008	0.568		28.88	0.0064
para-Xylene	2.018	0.571		28.33	0.0064
Petroleum ether	2.042	0.579			
Carbon bisulphide	2.057	0.580	25.37	31.38	0.0037
Acetone	2.112	0.590	27.0	23.50	0.0033
Ether	2.120	0.592	30.0	17.1	0.0024
Pentane	2.129	0.593	More than ether	About 15	0.0024

[1] NOTE.—The solubility of gases in these liquids increases in *general* with the per cent of compression or the compressibility, but the order is not exactly the same. The values for the density and for the pore volume listed in this table are calculated on the basis of the incorrect assumption that the liquids are incompressible. The same values would be obtained if the liquids are compressible but are not compressed.

When a tube containing the charcoal is outgassed, and mercury is admitted, this liquid fills what are technically known as the *voids* between the lumps, but we have found that it does not enter the very small *pores* in the lumps, so in this way the total volume of the lumps, and also the lump or "block" density, may be determined. For the charcoal given in table 1 this is 0.865. What is known as the apparent density of a charcoal is the mass of the charcoal contained in a 100 cu. cm. flask divided by 100, or it is the density of the carbon, pores, and voids, all taken together, and is usually about 0.5 for charcoals used by the Chemical Warfare Service. What is known usually as the "real density," though it is not the actual density, is that which is obtained by allowing water to penetrate the pores and by calculating the "real volume" of the carbon on the basis of the assumptions that the water completely fills the pores and that the water is not compressed by the attraction of the charcoal. The data of column 2 show that both of these assumptions cannot be correct. The densities of cocoanut shell charcoals as used by us when determined in water are 1.843 (table 1), 1.863, 1.835, and 1.808; that of the similar charcoal used, by Titoff,[1] 1.86; by Baerwald,[2] 1.92; and by Miss Homfray,[3] 1.66.

The compressibility data in table 1 are those of Bridgman,[4] those on surface tension were obtained in this laboratory, and the viscosity data, by different investigators. The compressibility increases in exactly the same order as either the pore volume or the density, except that the individual order for chloroform, benzene, and paraxylene is not known, though a study of Bridgman's curves of compression taken in connection with Richard's[5] data on their compressibility up to 500 atmospheres, makes the conclusion inevitable that as a class they lie between propyl alcohol and carbon bisulphide in accordance with their position in table 1. The curves plotted from Bridgman's data do not in general cross each other when all of the liquids are non-polar, while the curves for polar liquids not only cross each other, but also those for non-polar liquids.

The data indicate that the differences in the volume of liquid absorbed in 1 cu. cm. of the charcoal, listed as the pore volume in table 1, may be due either to the compressibility or the viscosity of the liquid, but on the whole they are in better agreement with the idea that it is the compressibility which is effective. The difference between the volume of ether and water absorbed is about 10%, and to produce this difference of volume by pressure exerted on the whole volume of liquid would require, according to Bridgman's data, between four and twelve thousand atmospheres. It is evident, however, that only a small fraction of the liquid is in actual contact with the charcoal. Dr. A. M. Williams[6] has calculated the volume of liquid in the primary film in the cocoanut charcoal used by Titoff as 0.30 ccm., which would be of the order of three-fifths of the pore volume. This would show that the average pressure in the primary film due to the

attraction of the carbon is extremely high, and while the difference between the compression of ether and that of water does not vary in such a way as to make it possible to give an exact estimate, the pressure would probably need to be more than *twenty thousand atmospheres* higher than the normal internal pressure of the liquid. The film, according to Williams, has an average thickness of 4×10^{-8} cm., which is of the order of one or two molecules in thickness for molecules of the dimensions used in our work. The magnitude of this pressure, which is the amount that the adhesional pressure betwen the carbon and the liquid *exceeds* that in the liquid itself, is not at all surprising. The deductions from the compressibility theory indicate, if the theory is on a sound basis, that the average pressure given in our experiments is of the order of twice to three times as great as the highest pressures obtained by Bridgman.

This theory leads to low values for the density of active carbon, or a density of about 1.6. Some of the charcoals which we have studied do not absorb more ether than they do water, or this compressive effect seems wanting. These are just the charcoals which are extremely inefficient in adsorbing gases, that is, cedar wood charcoal, with a density of 1.50, and beechwood charcoal with a density of 1.65, which values are of the same order of magnitude as that calculated for cocoanut shell charcoal, or as the density in water of the rather low-grade cocoanut shell charcoal used by Miss Homfray. A charcoal made from anthracite coal alone has a density of 1.876 in water, and only 1.906 in ether, while a sample of carbonite (made from anthracite and pitch) of 19 minutes accelerated chlorpicrin test had a density of 1.934 in water and 2.075 in ether.

The data of table 1 suggest still another theory, that the differences in the volumes of the liquids absorbed are due to their viscosity, the idea being that some of the pores are so fine that the liquids which are more viscous are less able to penetrate than those which are more fluid, at least in the time allowed for penetration, from 24 to 48 hours. The first results which we obtained indicated that the quantity of liquid absorbed increases with the time, but this time effect disappeared when we adopted the extremely thorough method of outgassing previously described. We have heard that Professor Hulett of Princeton University has found such a time effect, but presumably on less highly outgassed charcoals. Mr. Monroe is now engaged in a study of this effect under the conditions used in our tests. The principal evidence against the viscosity theory to be found in the data of table 1, is that the viscosity value obtained for propyl alcohol is badly out of order, since propyl alcohol is twice as viscous as water, yet much more of the propyl alcohol penetrates the pores. This accords exactly with the compressibility theory.

Experiments on the heat of adsorption of liquids gave some interesting results. A highly outgassed cocoanut shell charcoal gave a heat of adsorption equal to 10.5 calories per gram of charcoal when immersed in water

enough to completely fill its pores and voids. The same charcoal dried for ten days at 120 to 150° C., and then cooled over phosphorus pentoxide, had a smaller heat of adsorption, 7.0 calories, while it gave only 3.5 calories when it held a thin film of water equal to 0.04 gram per gram of charcoal. Thus the first tenth of the water which penetrates the pores gives rise to nearly all of the evolution of heat. Such experiments as this are now being carried out by precise methods, carefully measuring each amount of water added, in somewhat the same way as Titoff carried out his experiments on the heat of adsorption of gases, but with a number of added precautions. The results indicate that, in accord with the theory of Langmuir[7] and in agreement with the work of this laboratory on surfaces, the forces of adsorption or adhesion act only on an extremely thin layer of liquid.

The heat of adsorption of bone charcoal which had not been outgassed was found to be 18.5 calories, and in fullers' earth it was 32 calories, or almost the same values as were obtained by Gurvich[8] (18.5 and 30.2). Thus both of these solids have a very much higher heat of adsorption than even the best grades of cocoanut shell charcoal. While commonly known as the heat of adsorption, this is more precisely designated as the heat of spreading of a liquid on the surface of a solid. If $-Q$ is taken to represent the heat given off per square centimeter of surface; γ, the free surface energy; l, the latent heat of the surface; $-\Delta E$, the decrease of surface energy in spreading, and the subscript sp represents spreading; s, the solid, a and i, the interface, then

$$-Q_{sp} = -\Delta E_{sp} = \gamma_s + l_s - (\gamma_i + l_i). \qquad (1)$$

The adhesional heat and energy are defined by the equation

$$-Q_A = E_A = -\Delta E_s = \gamma_s + l_s + \gamma_l + l_l - (\gamma_i + l_i) \qquad (2)$$

or

$$-Q_{sp} = -Q_A - (\gamma_l + l_l). \qquad (3)$$

The heat of adsorption of enough gas to form a liquid in bulk, covering the solid surface at constant temperature (Q_T), is given by the equation

$$-Q_T = \gamma_s + l_s - (\gamma_i + l_i) + \lambda v \qquad (4)$$

where λ is the latent heat of vaporization of the liquid per unit volume of vapor. While we do not have the values of these quantities in the case of carbon, they have been determined in this laboratory for the interfaces between either mercury or water, and other liquids. The Pouillet effect, which is the heat given out when a liquid is adsorbed by a powder and is entirely analogous to that described here, has been attributed to the *compression* of the surface film of the liquid in contact with the powder. This compression, which was merely assumed from the standpoint of ideas on molecular attraction, is practically the same as that for which moderately direct evidence has been given in this paper. However, the above equations, which were developed by Harkins, show that the heat comes from

the total energy changes in the film, which include both the solid carbon and the liquid of the interface. This heat is entirely analogous to that developed when a body falls from a height above the earth to its surface, when the mutual potential energy of the body and the earth are converted into molecular kinetic energy, or heat. In a similar way, when the surface of the liquid and of the carbon fall together, their mutual potential energy of molecular attraction, due to electromagnetic (largely electrical) forces, is converted into molecular kinetic energy, which is heat.

This theory of the heat of adsorption has been developed by Harkins, but has not been published, although the fundamental equations upon which it is based have been published in these PROCEEDINGS. The final equations, (1) and (4), as given above, were not, however, presented. The experimental work on interfaces as carried out in this laboratory indicates that the γ_s of equation (1) is very large, and that most of the heat which appears is due to the fact that the interfacial free energy carbon-liquid is very much smaller than the free surface energy of the solid carbon. Equation (3) shows that the heat of adsorption of the liquid is equal to the energy of adhesion between the liquid and the carbon, minus the total surface energy of the liquid. In the case of water this total surface energy is moderately large, so the heat of spreading of the liquid is considerably less than the adhesional energy.

If further data agree with those already found in indicating that the differences in the volumes of various liquids absorbed by activated cocoanut shell and other highly activated charcoals are due to a compression by the forces of adhesion of the order of twenty thousand atmospheres as the average pressure in a film of 4×10^{-8} cm. in thickness, which would indicate a much higher pressure for the first layer of atoms, then the results presented in this paper will be the first direct evidence of the existence of such high forces between solids and liquids, or in liquids. Thus, while the theories of Laplace and van der Waals indicate an internal pressure of 10,000 atmospheres in water, and usually from 200 to 4,000 atmospheres in an organic liquid, it has not been found possible to demonstrate experimentally forces greater than 34 atmospheres with water at 24.4° C., 39.5 atmospheres for ethyl alcohol at 22.5, and 72 atmospheres for ether at 17.7°.[9]

The area of the surface in 1 gram of Miss Homfray's charcoal was 1.31×10^6 sq. cm. per gram of charcoal, and in Titoff's charcoal it was 8×10^6, according to estimates made by Williams.[2] Lamb, Wilson, and Chaney[10] have estimated the surface in a gas-mask charcoal as 10^7 sq. cm. per gram, or almost the same as in Titoff's charcoal. In this laboratory Mr. Amando Clemente has been working on the adsorption of vapors at low pressures, and his work seems to indicate an area very well in agreement with that of Lamb, Wilson, and Chaney, but experiments are still incomplete so the final value is uncertain. His work indicates that the adsorptive capacity

of charcoal at low pressures is greatly increased by repeated outgassing or by treating with the vapors or gases to be adsorbed several times between outgassings. Harned has noticed that in the latter way the speed of adsorption is increased, but the effect noticed here is on the equilibrium value. One gram of 750 minute charcoal, according to the ordinary chlorpicrin test, was outgassed, treated with benzene vapor, and then outgassed a second time. The volume of the whole apparatus was 2,200 cu. cm., and was filled at 24° with benzene vapor at a pressure of 1.5 mm. On opening this volume to the *one gram of charcoal*, the pressure fell in 12 hours to 0.00002 mm., or to less than *one seventy thousandth of the initial pressure*. The long time necessary was due to the fact that the equilibrium between the outside and inside of the lumps of charcoal is adjusted very slowly, since the diffusion is very slow. In a similar manner a pressure of 5.13 mm. was reduced to 0.00004 mm. In these experiments the charcoal was also at 24° C., so they illustrate the extremely great effect of the charcoal surface in increasing the life of the molecule[12] on the surface above what it would be on the surface of the liquid. In the second of these two experiments about one-tenth of the surface of the carbon was covered by molecules of benzene, provided the above estimates of the area of the surface are correct. On account of the great differences in the curvature of the surfaces of the pores, the different molecules are held by widely varying forces.

The apparatus first used in this work was similar to that described by Lemon,[11] but it was soon found that more rapid work could be done in an apparatus in which there are no stopcocks. Our work is the first which relates to the volume of different liquids taken up by charcoal. In addition to papers already cited, reference should be made to a paper by Chaney[12] on the activation of carbon, to papers by Langmuir[12] and by Harkins and his co-workers[13] on the theory of surfaces and adsorption, and to papers on adhesion by Harkins.[14] Thanks are due to Dr. Chaney for the preparation for special charcoals, and to the Gibbs Fund of the National Academy of Sciences for a grant which enabled us to purchase the vacuum apparatus.

[1] Titoff, *Zs. physik. Chem.*, **74**, 1910 (641).

[2] Baerwald, *Ann. Physik*, **23**, 1907 (84).

[3] Miss Homfray, *Zs. physik. Chem.*, **74**, 1910 (129).

[4] Bridgman, an extensive series of papers in *Proc. Amer. Acad. Arts Sci.*, especially **49**, 1913 (No. 1).

[5] Richards, *J. Amer. Chem. Soc.*, **38**, 1916 (989).

[6] Williams, *Proc. Roy. Soc. Edinburgh*, **38**, 1917–8 (23); **39**, 1918–9 (48); *Proc. Roy. Soc. London*, A **96**, 1919 (287 and 298).

[7] Langmuir, (*a*) *Met. Chem. Eng.*, **15**, 1916 (468); (*b*) *J. Amer. Chem. Soc.*, **39**, 1917 (1848); (*c*) *Ibid.*, **40**, 1918 (1361).

[8] *J. Russ. Phys. Chem. Soc.*, **47**, 1915 (805).

[9] Donny, *Ann. chim. phys.*, **16**, 1846 (167); Berthelot, *Ibid.*, (3) **30**, 1850 (232); Moser, *Ann. Phys.*, (2) **160**, 1877 (138); Helmholtz, *Ges. Abh.*, **3**, 1887 (264); Worthington,

London Phil. Trans., A **183**, 1892 (355); Meyer, *Zur Kenntnis des negativen Druckes in Flussigkeiten*, Halle, 1911.

[10] Lamb, Wilson, and Chaney, *J. Ind. Eng. Chem.*, **11**, 1919 (420).

[11] Lemon, *Physic. Rev.*, **14**, 1919 (283).

[12] Chaney, *Trans. Amer. Electrochem. Soc.*, 1919 (Advance sheets).

[13] Harkins, Brown, and Davies, *J. Amer. Chem. Soc.*, **39**, 1917 (354); Harkins, Davies, and Clark, *Ibid.*, (541); Harkins and King, *Ibid.*, **41**, 1919 (970); these PROCEEDINGS, **5**, 1919 (152).

[14] Harkins, these PROCEEDINGS, **5**, 1919 (December).

CENTRAL AMERICAN CALENDARS AND THE GREGORIAN DAY

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The day-for-day correlation of the Mayan, Aztecan, and Gregorian calendars depends upon mathematical relations and logical assumptions.

First, as regards the archaic Mayan system of counting time, seen in inscriptions on monuments, the following assumptions are regarded as established:

a. That the permutation cycle of 260 days made by combining 20 days and 13 numbers in sequence was continuously applied to days from a beginning day.

b. That the notational system by which the index number of a day was written down was also continuously applied and that the designation of a day in the permutation and in the notation was constant and determinable.

c. That the *tun* (360 days) and *katun* (7200 days) were not abstract time periods but instead were order values in the notational system and necessarily involved a context of the long count of days of the Mayas just as '06 or '19 necessarily involves a context in the long count of years that distinguishes European chronology.

d. That the Mayan *haab* was a vague year of 365 days divided into 18 long months of 20 days each and one short month of 5 days and that while the true length of the tropical year was known with tolerable accuracy to the Mayas no correction was directly applied to the *haab* count for fear of disorganizing the day count which was the common measure of all astronomical and mathematical cycles.

As regards the records and time counts used by the Mayas of northern Yucatan at the time of the Spanish conquest it is regarded as proven:

a. That an organic contact with the archaic long count was maintained through the orderly succession of *tuns* and *katuns* designated by the name of the day on which they were completed.

b. That a true contact and correlation of the U Kahlay Katunob cycle of the historical summaries in the Books of Chilan Balam and the archaic